

International Conference on Oil and Gas Engineering, OGE-2016

## The nitrogen oxide formation studying at natural gas combustion in non-circular profile furnaces of fire-tube boilers

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### Abstract

The chemical reactions and mathematical model accompanying the thermal, prompt and fuel nitrogen oxides emergence are presented in the paper. The furnace profile changing is a type of passive methods making it possible to decrease NO<sub>x</sub> concentration by means of gas flow velocity increasing, average temperature of gas mixture in the furnace decreasing and through the recirculation processes. The graphical study results in the form of variables characterizing ecological efficiency are represented.

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Peer-review under responsibility of the Omsk State Technical University

**Keywords:** combustion; nitrogen oxides; thermal; prompt; fuel; furnace; fire-tube boiler

### 1. Introduction

In the process of social production a man influences the environment and this is one of the main current problems. The fossil fuel combustion process is connected with air pollution therefore the boiler operation efficiency is now considerably determined by the environmental requirements [1, 2, 3]. Nitrogen oxides NO<sub>x</sub> are the main toxic components generated in the fuel combustion process [1, 3]. Nitrogen oxides which are approximately 10 times more dangerous than carbon monoxides, constitute the greatest danger under the fossil fuel combustion [2, 3].

During the fossil fuel combustion process in gas-tube boilers furnaces, nitrogen contained in the air and fuel actively interacts with oxygen to form nitrogen oxide NO, dinitrogen oxide N<sub>2</sub>O, and nitrogen dioxide NO<sub>2</sub>. The most of NO<sub>x</sub> produced in the exhaust products combustion process (95-99 %) in gas-tube boilers furnaces accounts for nitrogen monoxide NO. Other nitrogen oxides are formed in less amount.

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The profiled furnaces are studied insufficiently. The data of the theoretical studies at the furnace profile shape changing; rectangular, square, circle, horizontal and vertical ellipses showed that the fire-tube boiler having the furnace with the vertical ellipse profile shape has NO minimum concentration at the furnace outlet. In relation to the circle, NO outlet concentration is lower and able to amount to 23 % [4]. However, there is no data about the major semi axis - minor semi axis ratio influence on the nitrogen oxides formation process.

## 2. The study subject (Model, Process, Device, Synthesis, Experimental procedure, etc.)

The study subject of nitrogen oxides formation is a fire-tube boiler having the vertical ellipse cross section shape furnace at the different major semi axis  $a$  - minor semi axis  $b$  ratio (Fig.1). The furnace with the circle cross-section shape is the base model, upon that the comparisons will be made with its characteristics.

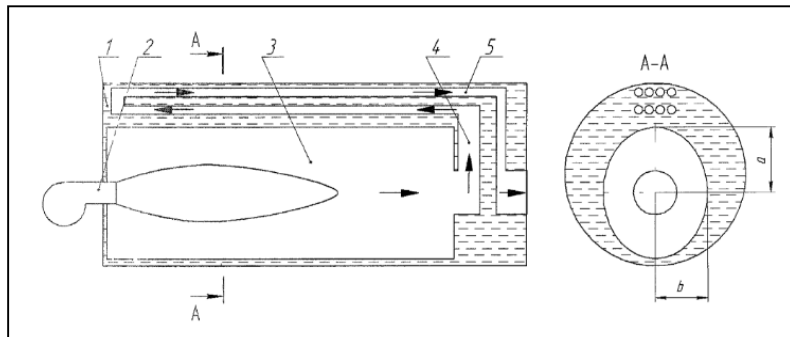


Fig.1. Then object scheme: 1 – water chamber; 2 – burner; 3 – furnace; 4 – reversing chamber; 5 – convection tube bank;  $a$  – major semi axis;  $b$  – minor semi axis.

Mass fraction  $\text{NO}_{\text{ellipse}}$  / mass fraction  $\text{NO}_{\text{circle}}$  [1] ratio at the furnace outlet for the furnaces with vertical ellipse and circle shape cross section correspondingly was chosen as the values characterizing the furnace ecological efficiency.

## 3. Methods

The necessary stage of high-temperature processes modelling in power installation units is the chemical effect kinetic diagrams construction. In general, the kinetic diagram represents a set of elementary chemical reactions describing the working body components conversion process.

The gaseous fuel combustion is described by the following reaction:  $\text{CH}_4 + 2\text{O}_2 = \text{CO}_2 + 2\text{H}_2\text{O}$ .

In the given reactions one substance is combined with another one in strictly defined quantities. These quantities are regulated by the stoichiometric ratio for reversible and irreversible reactions being performed for one stage [4, 5],

$$\sum_{I=A,B,C,\dots}^{N_C} V'_{KI} I \Leftrightarrow \sum_{I=A,B,C,\dots}^{N_C} V''_{KI} I \quad (1)$$

where  $N_C$  is the quality of reacting components;

$V_{KI}$  are the stoichiometric coefficients for  $I$ -component in the elementary reaction  $K$ .

The velocity  $S_I$  of  $I$ -component forming is calculated as follows:

$$S_I = W_I \sum_{K=1}^K (V''_{KI} - V'_{KI}) R_K \quad (2)$$

where  $W_I$  is the molar weight of  $I$ -component;

$$R_K = (F_K \prod_{I=A,B,C,\dots}^{N_C} [I]^{r'_{KI}} - B_K \prod_{I=A,B,C,\dots}^{N_C} [I]^{r''_{KI}}) \quad (3)$$

where  $R_K$  is the velocity of direct elementary reaction with  $I$ -component involvement;  $[I]$  is the  $I$ -component molar concentration;  $r'_{KI}$  is the  $K$ -reaction order for  $I$ -component.

$$F_K = A_K T^{\beta_K} \exp(-\frac{E_K}{RT}) \quad (4)$$

$$B_K = A_K T^{\beta_K} \exp(-\frac{E_K}{RT}) \quad (5)$$

where  $F_K$ ,  $B_K$  are the velocities constants of the reversible and irreversible reactions correspondingly (the Arrhenius equation);  $A_K$  is the preexponential factor;  $\beta_K$  is the coefficient depending on the temperature;  $E_K = 124024$  kJ/kmol is the activation energy;  $R$  is the gas constant;  $T$  is the temperature [5],  $A_K \cdot T^{\beta_K} \approx 1.0$  for homogeneous mixtures.

Subsequently, the main equations describing the reacting gas mixture under the following principal assumptions will be considered [1, 4, 5]:

- the heat from the flame to the wall is transferred by the radiation and convective heat transfer;
- inside the boundary layer the pressure does not change along the normal to the body circuit and is equal to the corresponding pressure on the boundary layer external edge;
- the total heat transfer on the gas mixture - wall boundary line is performed by means of the convective heat transfer and radiation;
- the reacting gas  $\text{CH}_4$  – 100 %, oxidizer is air.

The computational region is shown in Fig. 2.

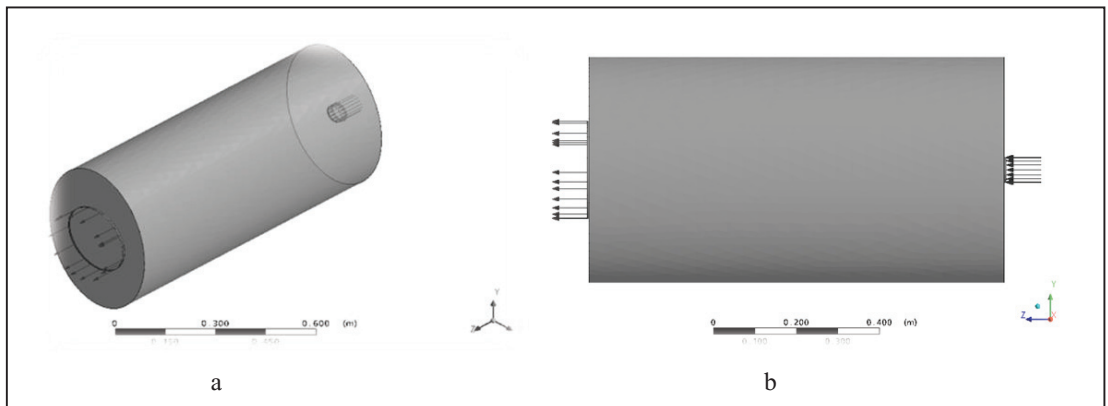


Fig.2. The furnace computational models: a - in the volume, b - the side view.

1. The continuities for all the mixture:

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{U}) = 0 \quad (6)$$

where  $\rho$  is the gas mixture density;  $\mathbf{U}$  is the velocity vector;  $t$  is the time.

2. The continuities for every component:

$$\frac{\partial(\rho Y_I)}{\partial t} + \frac{\partial(\rho u_j Y_I)}{\partial x_j} = \frac{\partial}{\partial x_j} \left( \Gamma_{Ieff} \frac{\partial Y_I}{\partial x_j} \right) + S_I \quad (7)$$

where  $S_I$  is the velocity of  $I$ -component forming;  $Y_I = \rho_I/\rho$  is the concentration of  $I$ -component substance;  $\rho_I$  is the density of every  $I$ -component;  $\Gamma_{ieff} = \Gamma_i + \mu_t/S_{ct}$  is the diffusion coefficient;  $\Gamma_I$  is the diffusion coefficient for  $I$ -component;  $\mu_t$  is the dynamic viscosity turbulent component;  $S_{ct} = \nu/\Gamma_I$  is the Schmidt number;  $\nu$  is the kinematic viscosity.

3. The moments:

$$\frac{\partial \rho U}{\partial t} + \nabla \cdot (\rho U \otimes U) - \nabla \cdot (\mu_{eff} \nabla U) = -\nabla P' + \nabla \cdot (\mu_{eff} \nabla U)^T + B \quad (8)$$

where  $B$  is the sum of all the forces acting upon the gas volume;  $\mu_{eff}$  is the efficient turbulent viscosity;  $P'$  is the pressure.

4. The energies and dissipations:

$$\frac{\partial (\rho k)}{\partial t} + \nabla \cdot (\rho U k) = \nabla \cdot \left[ \left( \mu + \frac{\mu_t}{\sigma_k} \right) \nabla k \right] + P_k - \rho \varepsilon - S^R \quad (9)$$

$$\frac{\partial (\rho \varepsilon)}{\partial t} + \nabla \cdot (\rho U \varepsilon) = \nabla \cdot \left[ \left( \mu + \frac{\mu_t}{\sigma_\varepsilon} \right) \nabla \varepsilon \right] + \frac{\varepsilon}{k} (C_{\varepsilon 1} P_k - C_{\varepsilon 2} \rho \varepsilon) \quad (10)$$

$$\nabla k = \frac{\partial k_x}{\partial x} + \frac{\partial k_y}{\partial y} + \frac{\partial k_z}{\partial z}, \nabla \varepsilon = \frac{\partial \varepsilon_x}{\partial x} + \frac{\partial \varepsilon_y}{\partial y} + \frac{\partial \varepsilon_z}{\partial z}$$

where  $S_R$  is the source term;  $C_{\varepsilon 1}$ ,  $C_{\varepsilon 2}$ ,  $\sigma_k$ ,  $\sigma_\varepsilon$  are the informative constants [5];  $P_k$  is the turbulence parameter characterizing the viscosity forces and buoyancy ones  $P_{kb}$  ratio [5]:

$$P_k = \mu_t \nabla U \cdot (\nabla U + \nabla U^T) - \frac{2}{3} \nabla \cdot U (3\mu_t \nabla \cdot U + \rho k) + P_{kb} \quad (11)$$

5. The enthalpy evaluation:

The total specific enthalpy  $h_{tot}$  is evaluated by the following formula:

$$h_{tot} = h + k$$

where  $h$  is the specific enthalpy of the stationary gas mixture.

6. The viscosity evaluation:

$k$ - $\varepsilon$  model is based on the turbulent viscosity conception, therefore

$$\mu_{eff} = \mu + \mu_t \quad (12)$$

where  $\mu$  is the dynamic viscosity.

7. The equation of state:

The equation of state offered by Redlich-Kwong is as follows [5]:

$$P = \frac{RT}{v-b+c} - \frac{a(T)}{v(v+b)} \quad (13)$$

where  $v$  is the specific volume. The values  $a$ ,  $b$ ,  $c$  are the constants depending on the substance [5].

8. The initial conditions:

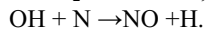
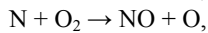
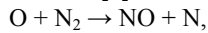
The parameter values included in the system of equations at the time of  $t = 0$  and at the initial temperature of  $T = 300$  K are accepted.

9. The corresponding boundary conditions are established.

The determination of nitrogen monoxide (oxide) formation under the fossil fuels combustion is conducted both as a result of air nitrogen  $N_2$  oxidation and contained in fuel nitrogen one. Nowadays there are three mechanisms,

whereby nitrogen oxides are formed: thermal, prompt, fuel ones. At the thermal and prompt NO formation, the source of nitrogen is the air and in case of the fuel NO formation it is nitrogen-containing fuel components [5], but taking into account the accepted assumptions the reacting gas  $\text{CH}_4$  is 100 %, the remained nitrogen oxides formation has not been studied.

The thermal nitrogen oxides formation mechanism was offered by Ja. B. Zeldovich and includes the following reactions[1]:



The reactions of thermal NO formation are characterized by the high activation energy, therefore, nitrogen oxides formation is carried out at the high temperatures exceeding 1800 K. The thermal NO concentration increases intensively in the combustion zone and achieves the largest values out of the maximum temperatures zone immediately. Henceforth, along the flame length the nitrogen oxides concentration practically does not change. The expressions for the velocities constants  $k$  for each of the three reactions are presented in the papers [1, 5] and are as follows:

$$k_1 = (1,8 \cdot 10^{11}) \exp\left(-\frac{38370}{T}\right)$$

$$k_2 = (6,4 \cdot 10^9) \exp\left(-\frac{3162}{T}\right)$$

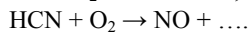
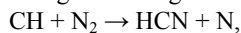
$$k_3 = 3,0 \cdot 10^{13}$$

The thermal NP formation is determined by the following principal factors: the temperature of the combustion area, the excess air coefficient and the combustion products dwelling time in the high temperatures zone. The thermal NO-component  $S_{\text{NO}, \text{thermal}}$  formation velocity is defined by the following formula:

$$S_{\text{NO}, \text{thermal}} = W_{\text{NO}} k_{\text{thermal}} [\text{O}] [\text{N}_2] \quad (14)$$

where  $k_{\text{thermal}} = 2k_1$ ;  $W_{\text{NO}}$  is the thermal NO molar mass;  $[\text{O}]$ ,  $[\text{N}_2]$  are the oxygen and nitrogen molar concentrations.

The hydrocarbon fuels studies conducted by Fenimore [1] revealed that in the flame front for a very short period of time the nitrogen oxides are formed by the mechanism different from the one offered by Ja. B. Zel'dovich. The found out nitrogen oxide was called a prompt one for the sufficiently high formation rate in the flame root section. In addition, near combustion zone a considerable amount of hydrogen cyanide HCN was observed due to molecular nitrogen reacting with hydrocarbons radicals:



The reactions of prompt oxides NP formation are performed vigorously enough at the temperatures of 1200-1600 K when thermal nitrogen oxides formation does not practically occur.

The formation velocity of prompt NO – component  $S_{\text{NO}, \text{prompt}}$  – is determined according to the following expression [73]:

$$S_{\text{NO}, \text{thermal}} = W_{\text{NO}} k_{\text{thermal}} [\text{O}] [\text{N}_2] [\text{Fuel}] (W/\rho)^{3/2} \quad (15)$$

$$k_{\text{prompt}} = A_{\text{prompt}} \exp(-T_{A \text{ prompt}}) / T \quad (16)$$

where  $A_{\text{prompt}}$  is the Arrhenius number.

#### 4. Results and Discussion

Further on, the presented above mathematical model [1] equations solutions results implemented in ANSYS CFX [5] are given.

The NO formation studies were conducted in the fire-tube boiler having the vertical ellipse cross section shape furnace at the different major semi axis  $a$  - minor semi axis  $b$  ratios. The furnace with circle cross-section shape is the base model, upon that the comparisons will be made with its characteristics.

The Reynolds numbers ratios  $Re_{ellipse}/Re_{circle}$  and nitrogen oxides mass fraction ratios at the furnace outlet (mass fraction  $NO_{ellipse}/\text{mass fraction } NO_{circle}$ ) [1, 5] for the furnaces with vertical ellipse and circle shape cross section correspondingly were chosen as the values characterizing the furnace efficiency.

Fig. 3 shows the dependency graphs  $\Theta = f(x/L)$ , where  $\Theta = (T_i - T_{\min})/(T_{\max} - T_{\min})$  ( $T_i$  is the average current temperature,  $T_{\min}$  is the minimum temperature,  $T_{\max}$  is the maximum temperature),  $x$  is the current coordinate and  $\tilde{V} = f(x/L)$ , where  $\tilde{V} = V_i/V_{ex}$  ( $V_i$  is the current velocity,  $V_{ex}$  is the furnace inlet velocity). The maximum temperatures and velocities ranges coincide and are found in the flame formation area.

The dependency  $Re_{ellipse}/Re_{circle} = f(a/b)$ , where  $Re_{ellipse}$  is the Reynolds criterion in the furnace with vertical ellipse shape cross section,  $Re_{circle}$  is Reynolds criterion in the furnace with circle shape cross section, is represented in Fig. 4. With  $a$  to  $b$  ratio increase up to  $\approx 1,3$ , the rising of  $Re_{ellipse}/Re_{circle}$  is observed as a consequence of velocity field deformation. Further increase of  $a/b$  results in the decrease of  $Re_{ellipse}/Re_{circle}$  due to the wall effects influence growth.

Simultaneously with the profile form changing and the  $Re$  number increasing, the nitrogen oxides mass fraction (mass fraction NO) decreases (Fig. 4) at the boiler furnace outlet which is achieved by the gas flow velocity increasing  $Re$ , gas flow average temperature  $T_{average}$  decreasing in the furnace and due to the recycling processes according to the equation:

$NO + \nu_F \text{Fuel} \rightarrow 1/2 N_2 + \nu(CO_2)CO_2 + \nu(H_2O)H_2O$ ,  
where  $\nu$  is the stoichiometric coefficient;  $Fuel$  is the fuel type[5].

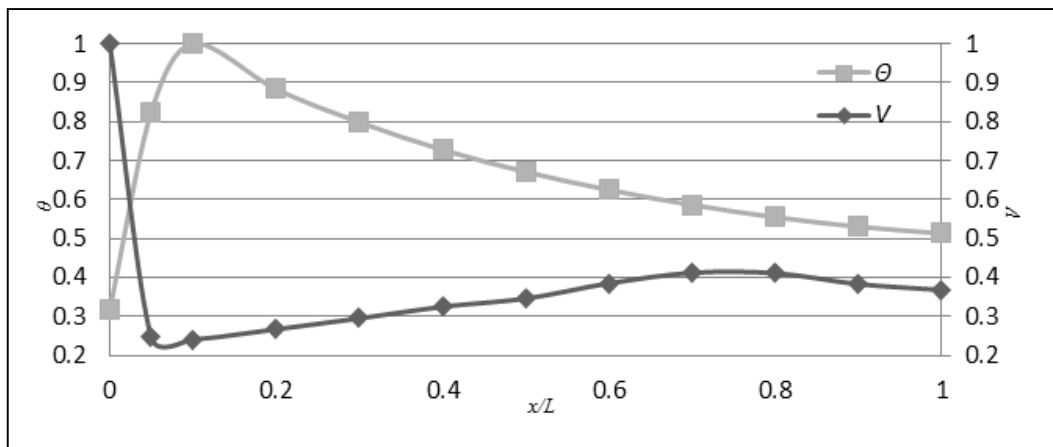


Fig.3. The temperatures and velocities distribution in the fire-tube boiler furnace along the furnace length.

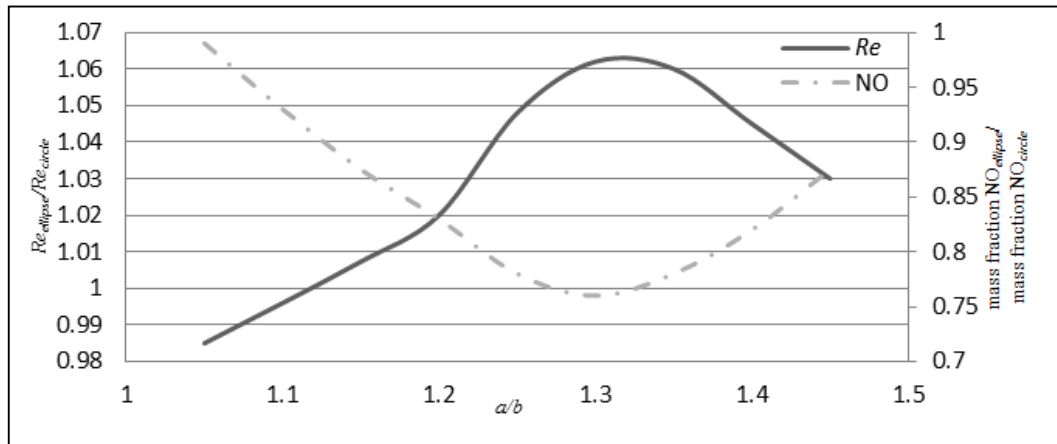


Fig.4. The  $Re_{ellipse}/Re_{circle}$  and  $NO_{ellipse}/NO_{circle}$  dependency on the  $a/b$  ratio.

## 5. Conclusion

Therefore, the furnace chamber cross section form changing from the circle to the elliptical one under the major semi axis - minor semi axis ratio within the range of 1,25-1,45 results in:

- 1) the heat flow convection component intensification, the Reynolds number increasing from  $92 \cdot 10^3$  up to  $93,5 \cdot 10^3$  specifically;
- 2)  $\eta$  rising within the range of 3,3 %;
- 3) NO mass fraction decreasing within the range of 23 %.

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